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Synthesis and Characterisation of Poliurethanic Hydrogel Based on Poly(2-ethyl-2-oxazoline) (PEtOx) and Polycaprolactone (PCL)

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Abstract

Polyurethanes are versatile materials, whose properties can be tailored by their composition. In this work, segmented polyurethanes based on poly(2-ethyl-2-oxazoline) and polycaprolactone, hydrophilic and hydrophobic segments, respectively, and biocompatible segments, were synthesized and characterized with respect to composition, thermal properties and swelling in water as a function of temperature and cell viability. The combination of these macrodiols resulted in amphiphilic, thermoresponsive and biocompatible polyurethanes.

Key words:

Polyurethane, Hydrogel, Thermoresponsiveness.

Introduction

PEtOx and PCL are biocompatible polymers, synthesized by ring opening polymerization, which results in polymers with controlled molar mass and narrow molar mass distribution.[1] PCL is a hydrophobic polymer, commonly used in biomedical applications, such as in regeneration of cartilaginous tissues, once its degradation time is similar to the tissue's regeneration. On the other hand, PEtOx is a hydrophilic and water-soluble polymer and its aqueous solutions are thermo- and pH-responsive, allowing applications such as drug carrier, separation systems, and so on.[2]

Polyurethanes (PU) are versatile polymers, whose properties can be easily tailored by composition and molar mass. The properties of the macrodiols precursors determine the properties of the PU. The combination of hydrophobic and hydrophilic blocks in a polyurethane chain leads to segmented and 'amphiphilic polymers and hydrogels, whose properties depend on the macrodiols ratio.[3]

Segmented polyurethanes were synthesised by using the two-steps route,[4] with variable PCL/PEtOx mass ratio. ^{1}H NMR and GPC were used for structural characterization. DSC and TGA allowed the evaluation of thermal transitions and thermal stability, respectively. Swelling measurements in aqueous solution were performed at different temperatures. Cell viability was evaluated with fibroblast cell line NHI 3T3 by MTS assay.

Results and Discussion

The characterisation by ^{1}H NMR and GPC allowed to obtain the effective composition of the PU, expressed in terms of PEtOx:PCL mass ratio, molar mass and polydispersity, as shown in Table 1.

Table 1. Effective PEtOx ratio in the PU, number and weight average molar masses and polydispersity (PDI).

PEtOx:PCL ratio (w)	%PEtOx (w/w)	Mn (kDa)	Mw (kDa)	PDI
1:0	100	12,9	25,1	2,0
3:1	90,4	33,0	132,5	4,0
1:1	61,2	17,9	46,0	2,6
1:3	39,1	29,4	72,0	2,5
0:1	0	39,6	95,3	2,4

Thermal analysis showed that the polymers are stable up to 200°C and degradation occurs in two main steps. The crystallinity provided by PCL segment is maintained PU richer in PCL.

The hydrogels were swollen with water and the water uptake increased according to the increase in the hydrophilic segment ratio (Figure 1). Temperature did not affect the swelling capability of the polyurethanes.

MTS assay (Figure 2) revealed that the PUs were not cytotoxic. The cell death in polyurethanes 50% and 25%PEtOx is due to residual DMSO present in the PU that could not be properly removed. Previous results showed that cell death decreased with DMSO removal.

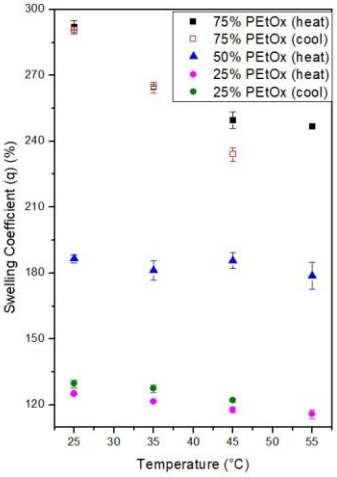

Figure 1. Swelling coefficient for heating and cooling cycles in aqueous media.

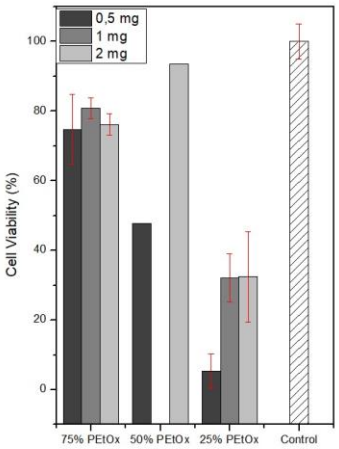

Figure 2. Cell viability for different polyurethane at different concentrations.

Conclusions

The PEtOx/PCL based polyurethanes presented composition close to the planed one and properties varying according to them. PUs richer in hydrophilic segment presented higher water content.

Cell viability assay allowed to investigate cytotoxicity, showing that the polyurethane 75%PEtOx is safe. The cell death observed is caused by residual DMSO in the materials.

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[1] Verbraken, B., Monnery B.D., Lava, K., Hoogenboom, R. *Eur. Polym. J.* **2017**, 88, 451.
[2] Hartlieb, M., Kempe, K., Schubert, U.S., *J. Mater. Chem. B* **2015**, 3, 1487.
[3] Loiola, L.M.D., Más, B.A., Duek, E.A.R., Felisberti, M.I., *Eur. Polym. J.* **2015**, 88, 451.
[4] Trinca, R.B., Felisberti, M.I., *Eur. Polym. J.* **2015**, 62, 77.